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Lime Treatment of 2,4,6-Trinitrotoluene Contaminated Soils: Proof of Concept Study

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ABSTRACT: Many active and formerly used Federal facilities contain areas where surface and subsurface unsaturated zone soils are contaminated with explosives. Currently there is no *in situ* treatment for stabilization, isolation, or remediation of soils impacted by military operations or manufacturing in support of military operations. The objective of the present work was to evaluate *in situ* lime treatment of TNT in soil. Bench scale studies were conducted using explosives-contaminated soil to determine the impact of mixing regimes and soil moisture content on TNT degradation using lime treatment. Various amounts of mixing and moisture were applied to replicate systems and analyzed for residual TNT and transformation products over time. Based on observations from the initial study, a follow-on bench scale experiment was conducted to assess the long-term rate and extent of TNT degradation using topical lime application. Results indicated that moderate lime application, consistent with agricultural standards, was sufficient for sustained treatment applications and 25 to 30 percent moisture content optimized TNT degradation kinetics. The present work clearly demonstrated that TNT could be degraded from contaminated soil by treatment with hydroxide ions in aqueous solution and by topical application of commercial grade lime in a static or mixed system. By assessing the effects of parameters critical to successful technology transfer, this effort provides an innovative technique for preventing the migration of surface and near surface soil contamination by TNT, which acts as a source zone for groundwater contamination on DoD testing and training ranges.

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, as part of cleanup technology development supported by the Environmental Quality Technology (EQT) Program.

Dr. Lance D. Hansen, Environmental Restoration Branch (ERB), and Drs. Jeffrey L. Davis and Steven L. Larson, Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC, and Ms. Catherine C. Nestler and Ms. Deborah R. Felt, Applied Research Associates, Inc., Vicksburg, MS, prepared this report. The Environmental Chemistry Branch, ERDC, performed the chemical analyses.

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COL James R. Rowan, EN, was Commander and Executive Director of ERDC, and Dr. James R. Houston was Director.

1 Introduction

Many active and formerly used Federal facilities contain areas where surface and subsurface unsaturated zone soils are contaminated with explosives. Contaminated lands are located in defined explosive production and handling facilities and as distributed sources on lands impacted by military operations, such as live-fire training ranges and impact areas. Three environmental concerns associated with this soil contamination are:

- a. Migration of the contamination through air and surface transport.
- b. Potential exposure of ecological receptors to the contaminant.
- c. Transport of explosives to groundwater with the contaminated soil acting as a source zone.

Currently no *in situ* treatment alternative is available for stabilization, isolation, or remediation of soils impacted by explosives residue generated by military operations or manufacturing in support of military operations. The costs to remediate these explosives-contaminated soils based on traditional *ex situ* methods far exceeds resources available for remediation. For the purpose of both remediation and prevention of contamination on an on-going basis, a cost-effective technology is required that is broadly applicable and may reduce the need for intensive on-site characterization.

In situ treatment of TNT in soil using lime is a promising alternative to traditional *ex situ* remediation methods. Using base hydrolysis on soils to remediate contaminated sites will reduce the overall costs of soil remediation by providing a technology capable of destroying explosives *in situ*, thereby eliminating the extensive capital costs and safety concerns associated with current *ex situ* remediation strategies. The technique is also applicable to on-going military training activities as a compliance/conservation method, thereby ensuring the long-term availability of training ranges and impact areas by minimizing or eliminating the potential for off-range migration of explosives/energetics.

The objective of the work presented here was to evaluate *in situ* treatment of TNT in soil using lime at bench-scale. Two parameters, mixing regime and soil moisture content, were studied in preliminary experiments. Mixing was selected as a critical technology parameter because of the operation and maintenance costs associated with physical handling. This parameter will perhaps be the most

critical in determining overall cost of restoration using this technology. The effect of various moisture concentrations on the transformation of TNT when challenged with a base in the form of agricultural lime was also selected as a critical parameter as a result of its possible impact on cost and/or rate of transformation. Additional maintenance costs may be incurred to maintain an optimal soil moisture level at the site but may be balanced by an increased degradation rate that shortens the remediation time. The results of this study indicated that TNT can be transformed in a static or mixed system with a moderate lime application in a matter of days. This implies that *in situ* treatment of TNT in soil using lime may offer an effective alternative to present remediation technologies.

Alkaline Hydrolysis of Explosives

The transformation of TNT in basic solutions has long been established (Janowsky 1891 and Urbanski 1964). Results of bench-scale experiments on TNT-contaminated water at the U.S. Army Engineer Research and Development Center (ERDC) validated complete transformation of dissolved TNT when challenged by hydroxide in sufficient concentrations (Felt et al. 2001a,b; Hansen et al. 2001). Aromatic ring cleavage and polymerization reactions were indicated. Early Microtox® screening results indicated that the final products of the hydroxide-TNT reaction had higher EC₅₀ levels (i.e., lower toxicity) than the parent compound. Microtox® EC₅₀ is the effective concentration where 50 percent of the expected fluorescence from the test bacterium, *Vibrio fischeri*, is inhibited. A UV/VIS spectroscopy study followed the hydroxide-TNT reaction in aqueous solution over time at wavelengths from 190 to 1,100 nm at four temperatures. Results from this study indicated that the hydroxide-TNT reaction required 48 hr to come to completion at room temperature in aqueous solutions, long after TNT itself had degraded (< 40 min)(Felt et al. 2002).

Other researchers have studied the effect of lime treatment on explosives-contaminated soil. Arienzo (1999) applied 1 percent calcium hydroxide (hydrated lime) to soil to produce hydrogen peroxide for the oxidation of TNT and found complete removal of TNT from soil in 10 min. Emmrich (1999, 2001) also treated TNT solutions and TNT-contaminated soils with calcium hydroxide at 20 °C. TNT transformation was described by a pseudo-first order rate constant with formation of both nitrite and nitrate as end products.

Agricultural and Engineering Uses of Lime

The application of lime to soil for agricultural or engineering purposes is a well-established practice. The following sections discuss lime formulations and their possible effects on soil chemistry and ecology. These factors should be considered when establishing site-specific requirements for this emerging technology.

Lime formulations

Different formulations of lime are available for agricultural and engineering use, each having different chemical and physical properties (Jones 1979). The two major divisions are the dolomitic (primarily magnesium-based) and calcitic (primarily calcium-based) lime. Basic agricultural lime is usually ground dolomitic lime unless the soil is calcium deficient. Agricultural addition of lime to soil is intended to achieve and maintain a neutral soil pH. Typical lime additions generally range from 2 to 29 tons per hectare. The information available for effects of liming on soil chemistry and ecology are based on pH 9 or less. As determined in aqueous studies, optimum TNT destruction occurs at pH 11 and higher. Future research must address the effects of high pH (>10) on surface and groundwater, soil chemistry and ecology, and plant growth.

The calcitic limes, hydrated lime (calcium hydroxide ($\text{Ca}(\text{OH})_2$)) and quicklime (calcium oxide (CaO)), are used primarily in engineering applications. Hydrated limes, with their different dissolution rates, are often used in wastewater treatment plants (Robinson and Burnham 2001). Quicklime and flyash (Class C flyash is 30 to 35 percent calcium oxide) are used in construction for soil stabilization of building foundations and roadbeds. In addition, each of these compounds is available in formulations that range from 20 to 40 percent aqueous slurries to pulverized to granular. In general, the greater the surface area, the faster the dissolution rate in water and the more effective the formulation at raising the pH. The sparingly soluble lime remains inert in soil, slowly dissolving in available water until it undergoes an acid/base reaction which neutralizes the alkali. This can occur naturally through reaction with acid soil components, or an acid produced by plant roots, or by reaction with an introduced chemical with a base dissociation constant (pK_b) higher than that of the alkaline lime species.

The cost-effectiveness of a particular lime formulation is often countered by efficiency, and it may be that a more expensive lime formulation will prove to be more efficient. For example, while both dusts and pellets react to raise the pH at about the same rate, lime pellets/granules may be more efficient because, even though they are generally more expensive, less is required (pounds/acre) to raise the pH over an extended period of time. Pellets are longer lasting in the soil than a dust, are also easier to handle, and are generally preferred for topical application. Dusts, on the other hand, don't require large amounts of water to release the hydroxide into soil pore spaces. Dusts are more evenly spread on the soil surface and are removed from the system rapidly. Therefore, lime selection for site treatment can be based on the following factors: the chemistry of the particular lime species, the type of application process/technology being used, the efficiency and effectiveness required in raising the pH, and the overall cost (Hart 1998; Murdoch 2002).

Effect of lime addition on soil chemistry

The soil chemistry that results from liming acid soils is different from the chemistry of inherently alkaline soils. The interactions between lime, fertilizer, and plants in an acid soil have been summarized by Kamprath and Foy (1985). An acid soil that is limed doesn't readily achieve the high pH found in a truly

alkaline situation. Liming an acid soil increases the effective cation exchange capacity of the soil. Aluminum and many of the heavy metals will precipitate out of solution, while others, such as molybdenum, will increase in solution. The concentration of sulfur dioxide (SO_4) in soil solution will also increase. The plant and fertilizer interactions that occur in an alkaline soil are reviewed by Kissel et al. (1985). In an alkaline soil, the soil chemistry is dominated by the concentration of calcium carbonate (CaCO_3) in the soil. Calcium carbonate influences the bioavailability of phosphorus, iron, zinc, sulfur, and nitrogen to the plants. Between pH 7.6 and 8.3, even the concentration of carbon dioxide in the atmosphere is able to affect the soil pH. When the soil pH climbs above 7, volatilization of ammonia can become significant if nitrogen fertilizer was previously applied.

Topical application of lime is common in no-till agricultural practices for increasing the pH of acidic surface and subsurface soils (Howard and Essington 1998). Smith et al. (1994) reported limited leaching of lime through the soil profile. Farina et al. (2000) found little vertical or horizontal movement of the alkalinity through the soil layers even when unreacted lime was visible in the soil. When a soil of neutral pH is limed, a portion of the light fraction of organic carbon is lost (Chan and Heenan 1999). However, limed soil was still able to achieve aggregate stability. The authors hypothesized that soil stability was caused by the formation of calcium bridges as new bonds between aggregates.

Effect of lime addition on soil ecology

Researchers have studied the effect of lime application on soil ecology, specifically effects on microbial communities, animal populations, and plants. Some bacteria, known as alkaliphiles, have adapted to life at high pH by modifying enzymes to function at $\text{pH} > 8$ (Acosta-Martinez and Tabatabai 2000). He et al. (1997) found that the addition of lime to acidic soil promoted microbial biomass. Simek et al. (1999) found that, over extended periods of time, the application of lime, with and without organic and inorganic fertilizers, increased the microbial biomass of the soil. Lime was also an important factor in the change in microbial community composition between organic and inorganic fertilizers. Bardgett et al. (1996) found that, while bacterial respiration and community composition were not immediately affected by reduced application of lime to pasture land, fungal community growth increased. Lime application may also influence earthworm populations. Most earthworm species prefer a soil pH around 7. If soil is acidic, then lime application promotes worm biomass (Lawson 2000).

The effect of alkaline pH on plants is a secondary effect of high pH on soil and microbial chemistry that alters the bioavailability of various minerals and metals. The effects of liming on root and shoot development were examined by Kerley (2000). At 2.5 percent CaO (w/w), combined lateral and taproot development was 57 percent less than in controlled soil (pH 7). However, the cluster root development was enhanced in limed soil. Shoot development was slower and some chlorosis was observed in high pH soil.

2 Materials and Methods

Experimental Design

To assess the application of lime as the base delivery technique for soil treatment, first, two engineering parameters were assessed at microcosm scale. This was followed by a bench-scale proof of concept study (Table 1). Mixing strategy and soil moisture content were identified as the parameters having the greatest impact on both application cost and effectiveness of treatment. Using mixing and moisture parameters identified in the preliminary experiments, a bench-scale experiment was conducted to more realistically determine field application rate and extent of contaminant degradation.

Table 1 Experimental Design			
Parameter	Sample Size	Moisture Content	Mixing
Mixing	5 g	31 percent by weight	3 treatments
Moisture Content	5 g	8 moisture contents	Rotated
Bench-Scale Proof of Concept	2,800 g	35 percent by weight	Initial mixing only

All soil for these studies was prepared by drying under forced air conditions in a 35 °C oven for 48 hr. Solid soil pieces were broken with a mortar and pestle and passed through # 40 sieve (0.0166 mm) for the preliminary experiments and through a #10 sieve (2 mm) for the bench-scale study.

Microcosm study

Three mixing regimes were assessed: static (the mixing control), rotated, and rotated with glass beads. The moisture content was determined for the soil. Each regime began with 5 g contaminated soil in amber 40-mL vials. The soil was combined with 5 percent dry lime (w:w). The vials were brought to 31 percent moisture (w:w) based on the initial soil moisture content. Glass beads were added to one-third of the vials and the experiment was separated into three assessments: static, rotated, and rotated with glass beads. Triplicate sacrificial replicates were analyzed at 0, 1, 3, 5, and 60 days for decreases in TNT and possible increases in transformation products. The rate and extent of degradation was compared in order to select a mixing regime to use for soil moisture assessments.

Eight soil moisture conditions were assessed. The moisture content of unamended soil was first determined. Each condition began with 5-g contaminated soil gravimetrically combined with 5 percent dry lime (w:w) in a 40-ml amber vial. Based on the original soil moisture, water was added at 0 (moisture control), 7.5, 15, 25, 50, 100, 150, and 200 percent (w:w) to achieve the eight study conditions. The experiments were run in triplicate. Based on results obtained from the previous mixing condition experiment, vials were rotated for 3 days after which samples were taken and analyzed for TNT and TNT transformation products.

Bench-scale study

Approximately 2,800 g sieved, contaminated soil from the Iowa Army Ammunition Plant was placed in a 9- × 13- × 2-in. stainless steel pan. This soil had a total organic carbon (TOC) of 1.2 percent, a cation exchange capacity (CEC) of 10.7 meq/100 g, and pH level of 7.6. Lime (5 percent (w:w)) was topically applied and mixed by stirring until visual observation confirmed uniform distribution. Water was topically applied to achieve 35 percent moisture (w:w) at a rate slow enough to prevent pooling or channeling. The pan was then covered to prevent photolysis. Triplicate 10-g soil samples were taken at 0, 1, 2, 3, 5, 10, 15, and 20 days to establish rate and extent of degradation under near field conditions.

Chemical Analysis

Soil samples were freeze-dried for 24 hr to remove moisture, combined with acetonitrile, and sonicated in a water-cooled bath for 18 hr. Representative aliquots of the acetonitrile phase were collected, diluted with an equal volume deionized water, and filtered through a 0.45- μ m syringe filter. Explosives concentration was determined by SW846 method 8330 (US Environmental Protection Agency (USEPA) 1994) using a Hewlett Packard 1090 equipped with a diode array detector (DAD) and C-18 reverse phase column. An isocratic mobile phase 50:50 methanol:water and a flow rate of 1 mL/min were used.

3 Results and Discussion

Mixing Regime Assessment

Data collected from this phase of the assessment indicated no significant impact of mixing on TNT degradation during the initial 2 days in the three treatment systems (Figure 1). TNT transformation during this period of the experiment probably represents early degradation of the soluble (available) fraction of TNT in the soil system. TNT molecules must be available in the aqueous phase when using lime treatment, as TNT must be exposed to the hydroxide ion for transformation.

After 10 days of treatment, TNT degradation in the mixed systems (8.1 percent initial TNT concentration remaining) was significantly greater ($p = 0.050$) than TNT degradation in the static system (18.1 percent initial TNT concentration remaining). The mixing effect may be caused by a combination of two factors:

- a. Mixing successfully distributed the hydroxide-laden water to pore spaces where TNT resided on particle surfaces.
- b. Mixing resulted in increased exposure of TNT depleted pore water to soil, resulting in increased transport to pore water where transformation could occur. The results would be overall lower detectable concentrations of TNT in the bulk soil matrix.

The addition of glass beads to rotated samples did not play a significant role in rate or extent of TNT transformation, as there was no significant difference between the two rotated treatments after 10 days. This could be due to the physical entrapment of the beads in the soil matrix or some physical/chemical characteristic of the soil.

An important outcome of this study is the overall reduction of TNT in static as well as mixed treatments. Kinetic results indicate that static treatments may require longer treatment times to reach levels achieved by treatments that include mixing regimes. Static treatment could, however, potentially be an effective method in certain locations where soil mixing would be undesirable or dangerous, such as live-fire ranges.

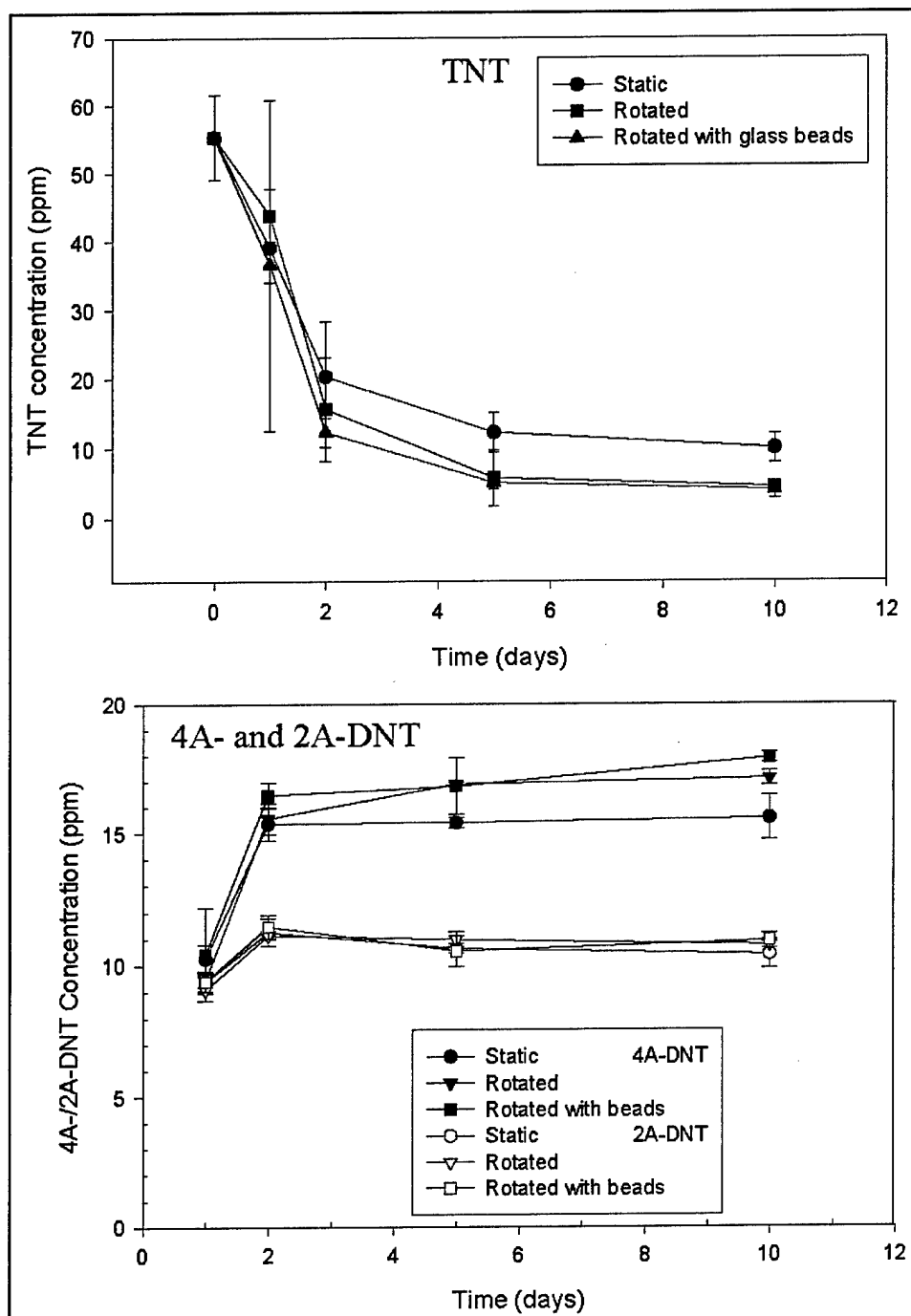


Figure 1. Comparison of mixing effects on explosives concentrations after treatment with agricultural lime

A small but significant increase in the concentrations of 2-amino-4,6-dinitrotoluene (2A-DNT) and 4A-amino-2,6-dinitrotoluene (4A-DNT) was evident in all three mixing regimes beginning at day 2. These compounds maintained the elevated concentration throughout the intermediate sampling points until the conclusion of the experiment at day 10 (Figure 1). This appears to indicate that 2A- and 4A-DNT were produced as a result of lime treatment of

TNT-contaminated soil. A mixing effect on 4A-DNT production was possible, since final 4A-DNT concentration was significantly lower ($p = 0.050$) in the static system compared to both rotated regimes. On this basis, no mixing effect on 2A-DNT production was observed, since no significant difference between the final 2A-DNT concentrations in the three systems was observed. The amounts of 2A-DNT and 4A-DNT produced after lime treatment of TNT represented less than 20 percent of the overall TNT transformed. Other known reduction products of TNT, such as diaminonitrotoluenes, were not detected in any of the systems assessed during this study.

One, or more, possibilities indicated by these results are:

- a. Chemical reduction of TNT is not a significant reaction step in base-induced transformation of TNT.
- b. Reductive transformation products may degrade quickly in this chemical system.
- c. Covalent bonding occurred between the soil organic matter and the transformation products as described by Thorn et al. (2002).

The kinetics portion of this initial study were of limited scope and therefore additional studies are necessary to assess possible transformation products that result from lime treatment of TNT contaminated soils.

Moisture Level Assessment

Figure 2 shows that an increase in moisture content up to 25 percent significantly affects the extent of TNT degradation. Optimal TNT degradation is achieved at or above approximately 25 percent moisture (w:w), and additional moisture content does not significantly impact the extent of TNT degradation ($p = 0.050$). Moisture content did not affect the production of 2A-DNT and 4A-DNT, as their production remained constant throughout this test.

Bench Pan Study Assessment

Following the initial microcosm assessment, a bench scale study was conducted to assess the transformation of TNT in contaminated soil when treated with agricultural lime. Soil representative of live-fire range contamination was used for the pan study. Figure 3 illustrates the results of the bench-scale study and confirms the proof of concept. TNT concentrations decreased over time after treatment with lime. The data were fit to a single exponential decay, $c = 0.933e^{-0.096t}$, where c is TNT concentration in parts per million, with an r^2 of 0.6002. The variance is rather high, but this is not unusual for soil data, which tend to be heterogeneous. By comparison, soil samples containing TNT that were not exposed to engineered alkaline conditions from lime application did not show significant reduction of TNT over a time course of 249 days (Figure 4).

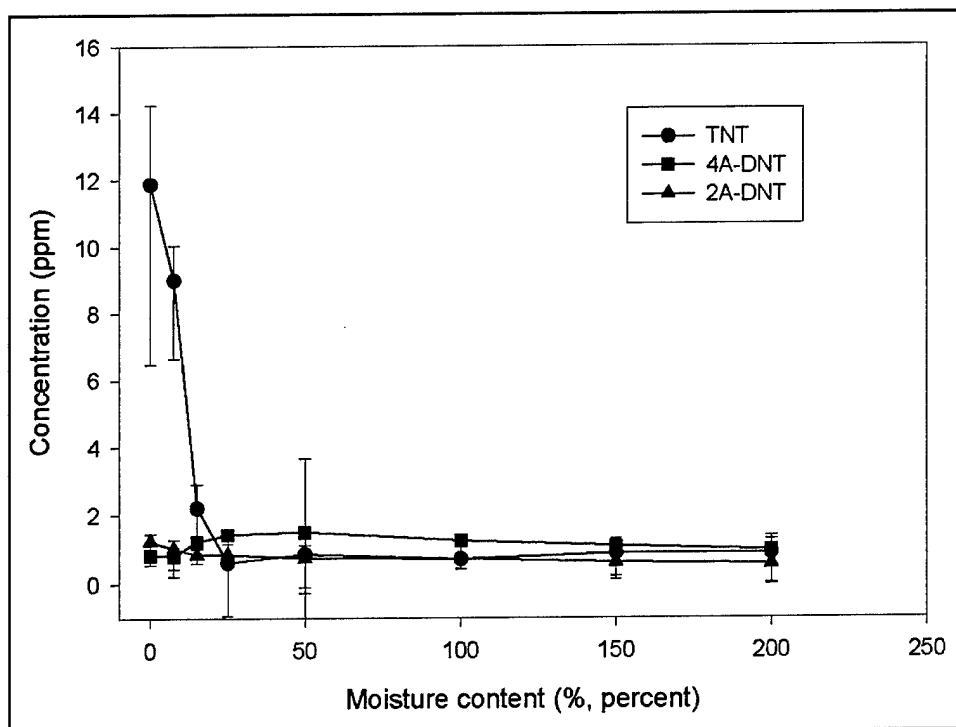


Figure 2. Effect of varying moisture on transformation of TNT

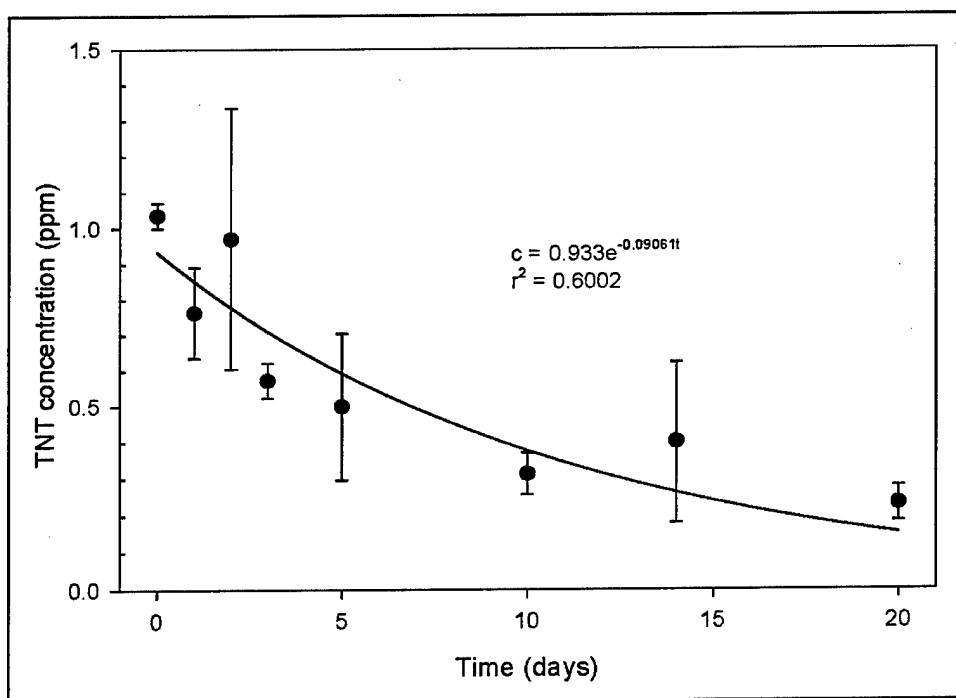


Figure 3. TNT transformation in proof-of-concept bench-scale study

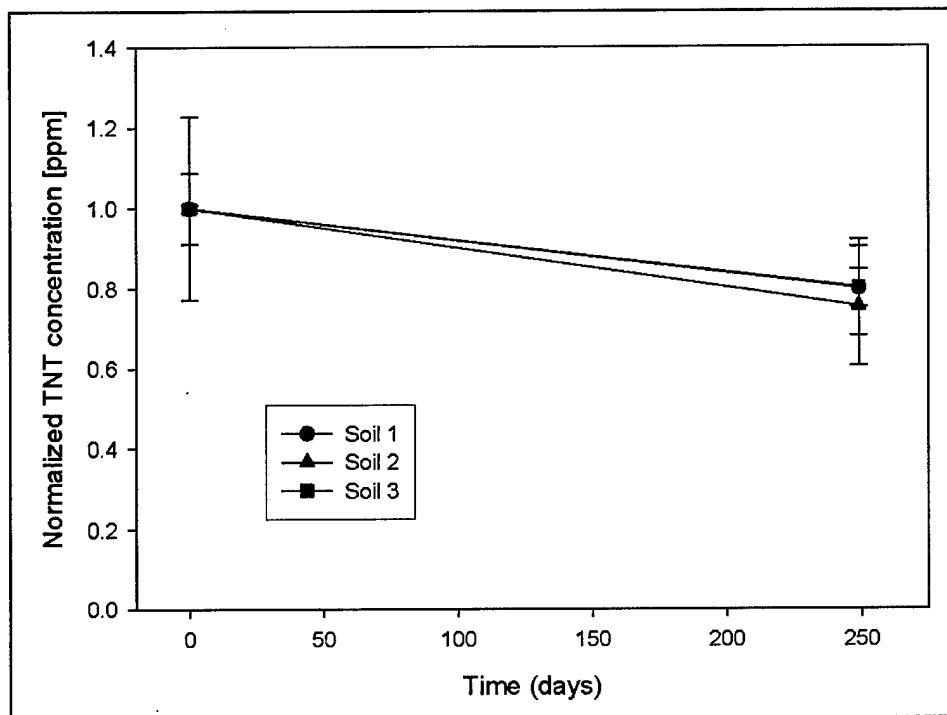


Figure 4. TNT profile in soil without alkaline treatment

These results indicate that TNT can be transformed in a static system with a moderate lime application in a matter of days. This information provides useful insight into applications for risk assessment and risk management strategies on TNT-contaminated lands. Additional studies are needed to assess long-term kinetics and any possible environmental impact of lime treatment of explosives-contaminated soils.

Future Work

Future work plans include a more complete identification of the transformation products produced by the TNT-hydroxide reaction. Both the mobility of these products through the soil and their toxicity will be established. Soil recovery after treatment with agricultural lime will be assessed. Results will be integrated into development of treatment protocols to accommodate optimal land use patterns for military relevant activities. Surface water runoff and groundwater transfer will be examined to determine the effects of elevated pH on cross-media migration of transformation products.

RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazine) are usually co-contaminants with TNT along with a number of propellants and transformation products. Heilmann et al. (1996) indicated that both HMX and RDX were susceptible to degradation by alkaline attack. Future studies should also consider the presence of these compounds during the development of site remediation strategies.

4 Conclusions

Previous work conducted by Felt et al. (2001a and b, 2002), and Hansen et al. (2001), demonstrated transformation of TNT in aqueous solution. The present work clearly demonstrated that TNT could be degraded from contaminated soil by treatment with hydroxide ion in aqueous solution as well as from topical application of commercial grade lime. This series of studies demonstrated that:

- a.* TNT can be destroyed in static systems demonstrating the potential for remote restoration of contaminated live-fire ranges.
- b.* Moderate lime application, consistent with agricultural standards, is sufficient for treatment applications.
- c.* Moisture addition of approximately 25 to 30 percent, or greater, optimizes TNT degradation kinetics.

By assessing the effects of parameters critical to successful technology transfer, this effort provides an innovative technique for treating near-surface soil contamination by TNT, which acts as a potential source zone for groundwater contamination on DoD testing and training ranges. By developing data that were previously unavailable, this work improves the state of the science and technology of environmental restoration for military unique compounds.

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14. ABSTRACT Many active and formerly used Federal facilities contain areas where surface and subsurface unsaturated zone soils are contaminated with explosives. Currently there is no <i>in situ</i> treatment for stabilization, isolation, or remediation of soils impacted by military operations or manufacturing in support of military operations. The objective of the present work was to evaluate <i>in situ</i> lime treatment of TNT in soil. Bench scale studies were conducted using explosives-contaminated soil to determine the impact of mixing regimes and soil moisture content on TNT degradation using lime treatment. Various amounts of mixing and moisture were applied to replicate systems and analyzed for residual TNT and transformation products over time. Based on observations from the initial study, a follow-on bench scale experiment was conducted to assess the long-term rate and extent of TNT degradation using topical lime application. Results indicated that moderate lime application, consistent with agricultural standards, was sufficient for sustained treatment applications and 25 to 30 percent moisture content optimized TNT degradation kinetics. The present work clearly demonstrated that TNT could be degraded from contaminated soil by treatment with hydroxide ions in aqueous solution and by topical application of commercial grade lime in a static or mixed system. By assessing the effects of parameters critical to successful technology transfer, this effort provides an innovative technique for preventing the migration of surface and near surface soil contamination by TNT, which acts as a source zone for groundwater contamination on DoD testing and training ranges.					
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